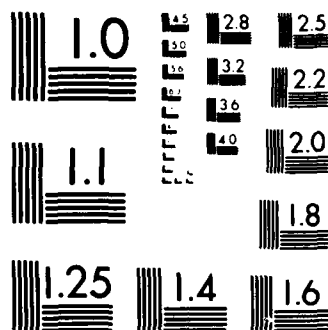


AD-A188 874      COMPARISON OF JFTOT HEATER TUBE DEPOSIT RATING METHODS      1/1  
FOR THE EVALUATION OF FUEL THERMAL STABILITY(U) NAVAL  
RESEARCH LAB WASHINGTON DC      R E MORRIS ET AL. 29 DEC 87  
UNCLASSIFIED      NRL-MR-6147      F/O 21/2      NL





MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

2



# Naval Research Laboratory

Washington, DC 20375-5000

NRL Memorandum Report 6147

**AD-A188 874**

**DTIC FILE COPY**

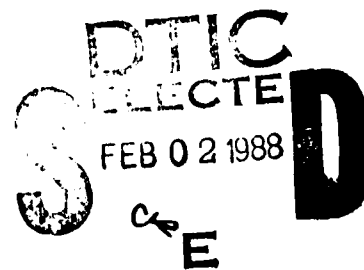
## **Comparison of JFTOT Heater Tube Deposit Rating Methods for the Evaluation of Fuel Thermal Stability**

ROBERT E. MORRIS, ROBERT N. HAZELTT,  
AND C. LINDEN MCILVAINE III\*

*Navy Technology Center for Safety and Survivability  
Chemistry Division*

*\*Geo-Centers, Inc.*

December 29, 1987



Approved for public release; distribution unlimited.

88 1 27 036

## REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		Approved for public release; distribution unlimited.	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)  NRL Memorandum Report 6147		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION  Naval Research Laboratory	6b. OFFICE SYMBOL (If applicable)  Code 6180	7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code)  Washington, DC 20375-5000		7b. ADDRESS (City, State, and ZIP Code)	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Chief of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) 800 Quincy Street Arlington, VA 22217-5000		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO 62233N	PROJECT NO TASK NO WORK UNIT ACCESSION NO
11. TITLE (Include Security Classification) Comparison of JFTOT Heater Tube Deposit Rating Methods for the Evaluation of Fuel Thermal Stability			
12. PERSONAL AUTHOR(S) Morris, Robert E., Hazlett, Robert N., and McIlvaine, C. Linden			
13a. TYPE OF REPORT Interim	13b. TIME COVERED FROM 7/86 TO 6/86	14. DATE OF REPORT (Year, Month, Day) 1987 December 29	15. PAGE COUNT 18
16. SUPPLEMENTARY NOTATION Geo-Centers, Inc.			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		Jet fuels	
		Tube deposit rating methods	
		Thermal oxidation stability, JFTOT	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>Quantification of deposits formed of heated metal surfaces is desirable for the evaluation of thermal stability by the JFTOT procedure. Empirical methods widely employed entail either visual comparisons or measurements of reflected light (TDR), both of which are sensitive to deposit color. We have examined these and several other measurement techniques for JFTOT heater tubes and have found that measurements of total carbon content by combustion were the most reliable. Two novel techniques, based on measurements of dielectric strength and interference effects of monochromatic light have been examined. It was found that the dielectric and interference methods correlated well with the combustion analyses and each other, while the TDR often yielded misleading results. The correlations between the various methods will be discussed in addition to the consequence of method choice on the interpretation of experimental data.</p>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS REPORT <input type="checkbox"/> EXT. REFS.		21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL R. E. Morris		22b. TELEPHONE (Include Area Code) (202) 767-3847 Code 6180	

# CONTENTS

Page No.

INTRODUCTION.....	1
EXPERIMENTAL.....	2
JFTOT Runs.....	2
Tube Deposit Measurements.....	3
DISCUSSION.....	4
CONCLUSIONS.....	5
REFERENCES.....	6

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

## COMPARISON OF JFTOT HEATER TUBE DEPOSIT RATING METHODS FOR THE EVALUATION OF FUEL THERMAL STABILITY

### INTRODUCTION

The property of thermal oxidation stability describes the extent to which thermally induced decomposition occurs in the fuel. This process is often accompanied by the formation of insoluble reaction products, either as a precipitate or as a gum which adheres to container surfaces. Modern aircraft engine designs and aerodynamic heating of wing surfaces place more severe thermal stress on the fuel, increasing the likelihood of the formation of insoluble deposits. Aircraft fuel system deposits can be responsible for a variety of problems including decreased efficiency of engine heat exchangers, seizing of fuel control valves and injector fouling.

It is known that thermally initiated fuel degradation is accelerated by the presence of oxygen through autoxidative processes involving free radical chain reactions. The Jet Fuel Thermal Oxidation Tester (JFTOT) has been widely used for the characterization of thermal oxidation stability of a fuel. In the JFTOT, aerated fuel is pressurized with nitrogen and passed over a heated metal tube so that the fuel is stressed under conditions of high oxygen availability and slowly increasing temperatures. The quantities of insoluble products formed under these conditions constitute a measure of the deposit forming characteristics of the fuel. In accordance with standard ASTM D3241 test procedures(1), the formation of filterable insolubles is detected from changes in pressure differential across a standard test filter downstream of the heated tube and the adherent insolubles are characterized by visual comparison with color standards. The highly subjective nature of the visual method of rating heater tube deposits was revealed in a round-robin effort conducted by the Coordinating Research Council(2). The poor precision of visual ratings from unusual and highly colored deposits resulted in random errors which were in excess of the differences between the values, thus eliminating any statistical significance. To increase the reliability of the measurement, the Tube Deposit Rating (TDR) was developed. The TDR is based on the attenuation of reflected white light from the coated heater tube. From comparisons with measurements of deposit thicknesses by Auger spectroscopy, Martel and Bradley(3) found that neither the Visual Rating method nor the TDR were adequate in rating tube deposits. While less subject to operator judgement than the visual rating method, the TDR can be influenced by the optical properties of the deposit.

Quantification of tube deposits by combustion of carbon to carbon dioxide has been investigated, with the assumption that carbon constitutes the majority of the deposits. Taylor(4) utilized measurements of total

carbon contents per unit area per unit time to study the influence of dissolved oxygen on the rates of deposit formation from thermally stressed jet fuels on 316 stainless steel tubes. The studies were later extended by Taylor(5) to examine the effects of trace amounts of sulfur-bearing compounds on deposition rates and by Taylor and Frankenfeld(6) to include nitrogen compounds. Giovanetti and Szetela(7) employed combustion analyses to quantify deposition rates from jet fuels stressed under a wide variety of experimental conditions in a special test apparatus. Carbon was determined from deposits on sintered stainless steel filters and from the inner walls of heated 316 stainless steel tubes. A lower limit of 200 micrograms carbon on the tube sections was reported. Kendall and Mills(8) have shown that the precision of combustion analyses conducted on standard JFTOT heater tubes has been limited by the difficulty with which quantitative removal of carbon from the aluminum surface could be attained. They found that the amount of carbon from stainless steel tubes generally exceeded that from aluminum tubes by a factor of two. In addition, migration of magnesium in 6061 T6 alloy aluminum heater tubes at elevated temperatures, has been reported to catalyze deposition. Heater tubes comprised of 304 stainless steel do not form porous oxide coatings, allowing much lower detection limits, nor is magnesium catalysis possible. Besides these limitations associated with the use of aluminum tubes, the tubes are destroyed during the combustion analysis and it provides no detailed information concerning the spatial distribution of the deposit.

Two novel techniques for determining the volumes of heater tube deposits have been developed. One technique, developed by Stavinoha, et.al.,(9), is based on measurements of the electrical insulating properties of the deposit. The other method, developed by Darrah, et.al.,(10), is based on the interference effect produced when monochromatic light is reflected off the tube surface through the deposit. Since these methods are non-destructive, we were able to obtain deposit measurements from the TDR, dielectric, interference and combustion methods on each JFTOT heater tube. In this study, the results from the four methods are compared.

## EXPERIMENTAL

### JFTOT Runs

Thermal stressing of fuel samples was performed using the modified JFTOT described earlier by Hazlett, et.al.(11). Five-inch 304 stainless steel heater tubes were employed to achieve a more gradual increase in temperature, greater reactive metal surface area and to facilitate the combustion analysis. In order to ensure sufficient quantities of material for combustion analysis, run times were increased to 300 minutes. Under these conditions, at a maximum fuel flow rate of approximately three milliliters per minute, the residence time of the fuel in the heater tube holder was approximately 28 seconds. Appreciable amounts of filterable insolubles would substantially reduce the fuel flow rate through the test filter and increase the contact time of the fuel with the heated tube surface. As a result, the stress on the fuel would be increased beyond the normal limits of the test and erroneously high levels of insolubles

could be produced. Fuel flow rates were therefore maintained at or above 2.5 mL/min by bypassing the test filter when the flow rate dropped below that point. Tests were conducted at maximum heater tube temperatures of 260, 270, 280 and 310°C.

#### Tube Deposit Measurements

Spun TDR measurements were taken with an Alcor Mark 9 tube deposit rating device. The TDR is based on the measurement of the attenuation of reflected white light by a photocell; thicker coatings increase the TDR while a clean tube surface gives a reading of zero. The instrument was calibrated in accordance with the manufacturer's instructions, using a calibration tube supplied with the instrument having known reflectance coatings. Readings were taken on heater tubes before and after stressing at two millimeter intervals over the 120 mm heated length. To obtain a measure of the changes in reflectance due to the deposit, differences between the initial and final TDR values at each location were calculated. The sum of these TDR changes constituted the total delta TDR, which was used as an indication of the total amount of deposit on the tube.

Volume measurements were performed by Southwest Research, Inc., using their dielectric measuring device. Central to this technique are the assumptions that an organic deposit will behave as an electrical insulator and that all typical deposits have similar dielectric strengths. When a voltage potential is applied across the tube deposit, it acts as an electrical insulator until the potential reaches the level at which the organic material comprising the coating breaks down. At that point, the coating ceases to act as a dielectric insulator and current begins to flow through the coating. The dielectric breakdown was determined by increasing an applied voltage potential across the coating at a controlled rate while monitoring the current drain. Deposit thicknesses were calculated from an empirically determined(9) proportionality factor, which relates the dielectric breakdown voltage to deposit thickness. Since the potential was applied through a stylus which is placed on the outside surface of the coating, the precision of the measurement could be expected to be reduced with very thin coatings. The nature of the measurement precludes spinning of the tube to average out variations in thickness around the tube, so the side of the tube with the thickest coating was taken as a reference point i.e., zero degrees. Measurements were obtained at 2 mm intervals down the tube at 0, 90, 180 and 270 degrees, providing four sets of thickness measurements for each tube. At each location, the readings were averaged and used to calculate the total deposit volume.

Deposit thickness measurements by interferometry were obtained by Geo-Centers, Inc., using the apparatus they had developed. Monochromatic light having a wavelength of 680 nm was directed onto the coated tube in a direction perpendicular to the surface through a fiber optic assembly which contained both the source and detector optics. The light intensity measured in this technique represents the quantity of light which emerged through the coating after reflecting off the metal tube surface. Since there is a large difference in the refractive indices between the air and the deposit, the reflected light wave undergoes a phase change. As a



consequence, the emergent wave interferes constructively or destructively with the incident wave, depending on the thickness of the deposit. As the detector was scanned across a deposit, the light intensity changed periodically as the deposit thickness passed through multiples of the wavelength of the incident light. At thicker deposit thicknesses, absorption of the light by the coating dominated, limiting measurement to thicknesses below approximately two microns. Like the dielectric method, the interference method is also a static measurement which is conducted at four quadrants down the tube length, using the side having the thickest coating as the reference. The thicknesses at each tube location were averaged and used to calculate the total deposit volume.

Total carbon contents of the tube deposits were determined after completion of the other measurements. Combustion analyses were performed with a Perkin-Elmer model 240 elemental analyzer. After calibration of the analyzer with known compounds, blank values were obtained from cleaned, unused heater tube sections. The grip ends of the heater tubes were removed and the heated section was cut into two equal lengths, cleaned by soaking in toluene, and analyzed.

#### DISCUSSION

The quantities of total carbon from each JFTOT heater tube, the TDR values and the deposit volumes from the dielectric breakdown and interference methods are given in Table 1. The TDR values represent the summation of the differences between the spun TDR values along the heater tube before and after stressing. The entries in table 1 are arranged in order of decreasing carbon content and it can readily be seen that poor correlation was found between carbon content and TDR values. The scatter plot of TDR values vs total carbon in Fig. 1 illustrates that, although there is a tendency for the heavier deposits to exhibit higher TDR readings, there was a high degree of uncertainty. This illustrates the deficiency of the TDR when used quantitatively in research efforts undertaken with the JFTOT.

A plot of the deposit volumes calculated from the dielectric and interference measurements vs total carbon (Fig. 2), indicates that these quantities are more linearly related to carbon content than the TDR. Light absorption by the thicker deposits limited the useful range of the interference measurements to coatings containing less than 400 micrograms of carbon. Close examination of Fig. 2 reveals that deposit volumes calculated from dielectric breakdown measurements from thin deposits were somewhat less than corresponding determinations by the interference method. It is not possible on the basis of these data, to determine which method provides the best result for the thinner coatings.

Both of these two new non-destructive techniques provide a convenient means of measuring deposit thicknesses at known locations on non-spinning tubes. Such techniques could be employed to determine the relationships between deposit thickness variations and experimental variations. Thickness profiles from interferometry along four sides of a typical heater tube are illustrated in Fig. 3. In this example, the thickness measured at 0° was nearly twice that at 90 and 180°, where the side of the

tube having the thickest deposit was designated as 0° and the other profiles were taken by indexing the tube in 90° increments. In those instances where there are large radial variations in thickness, increasing the number of measurements around the circumference would increase the precision of the volume calculation. However, the high degree of correlation with the combustion data indicates that, in these experiments, the precision of the deposit volumes from measurements at four locations was comparable to that of the combustion data.

The degrees of correspondence between tube deposit measurements from these methods can be quantitatively expressed by performing regression analyses and considering the linear correlation coefficients. From the regression correlation coefficients given in Table 2 the deposit volumes by the dielectric breakdown and the interference methods are shown to correlate extremely well with total carbon contents and with each other. The TDR values did not correlate with any of the other measurements.

Typical TDR profiles from two heater tubes having maximum TDR values of 47 and 28 at the locations of maximum tube temperatures, are shown in Fig. 4. The TDR scan of the heavier deposit also contains a secondary maximum at approximately 80 mm. Comparison of the TDR plots with the corresponding maximum dielectric breakdown potentials of 828.3 and 17.2 volts from the same two tubes (Fig. 5) illustrates the increased range of the measurement over the TDR. This illustrates a case in which changes in TDR were not proportional to the actual quantities of tube deposits. Carbon contents of the entire deposits on these two tubes was 381 and 27 micrograms, respectively. The random nature of the correlation between TDR and carbon contents or deposit volumes renders the existence of any systematic non-linear relationship very unlikely. The secondary maximum at 80 mm was also not apparent from the dielectric measurements. This type of effect may have been caused by light absorption by a thin, highly colored deposit which resulted in an erroneously high TDR. There is also the possibility of interference effects arising from thin coatings with thicknesses in multiples of the dominant wavelength of the incandescent lamps used in the TDR rating device.

## CONCLUSIONS

Excellent agreement was obtained between JFTOT heater tube deposit volumes calculated from measurements of dielectric breakdown and from optical interference and the total amount of carbon measured by combustion. Tube deposit volumes calculated by the two non-destructive measurements could be used in place of total carbon measurements to make quantitative comparisons from 304 stainless steel heater tubes.

As practical alternatives to combustion analyses, the dielectric and interference methods may allow the use of aluminum JFTOT tubes in quantitative studies. These new techniques could also provide a convenient and practical means with which to study the relationships between fuel flow and deposit characteristics and to determine the influence of heater tube composition without resorting to combustion analyses to quantify deposits. The thickness profiles obtained by these two new methods have also demonstrated instances where the TDR values were

disproportionately influenced by thin, highly colored deposits. The failure of the TDR to respond proportionately to certain types of deposits poses limitations on its usefulness as a tool for quantitative measurements.

The precision of the volume calculations by the dielectric and interference methods can be affected by extreme radial variations in deposit thickness. Therefore, in those instances where higher precision is desired, it may be necessary to increase the number of measurements taken around the tube circumference.

#### REFERENCES

1. ASTM D3241-74, "Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure)", 1976 Annual Book of ASTM Standards, part 25.
2. Tube Deposit Rating Techniques Panel, "Investigation of Techniques for Evaluating Oxidative Stability Deposits of Aviation Turbine Fuel", CRC Project No. CA-43-67, October 1974, Coordinating Research Council, Inc., New York, New York.
3. C. R. Martel and R. P. Bradley, "Comparison of Rating Techniques for JFTOT Heater Tube Deposits", Interim Report No. AFAPL-TR-75-49, Air Force Aero Propulsion Laboratory, October 1975.
4. W. F. Taylor, "Deposit Formation from Deoxygenated Hydrocarbons. 1. General Features", Ind. Eng. Chem. Prod. Res. Dev., 13, p 133, 1974.
5. W. F. Taylor, "Deposit Formation from Deoxygenated Hydrocarbons. 2. Effect of Trace Sulfur Compounds", Ind. Eng. Chem. Prod. Res. Dev., 15, p 64, 1976.
6. W. F. Taylor and J. W. Frankenfeld, "Deposit Formation from Deoxygenated Hydrocarbons. 3. Effects of Trace Nitrogen and Oxygen Compounds", Ind. Eng. Chem. Prod. Res. Dev., 17, (1), p 86, 1978.
7. A. J. Giovanetti and E. J. Szetela, "Long Term Deposit Formation in Aviation Turbine Fuel at Elevated Temperature", NASA Report No. CR-179579, United Technologies Research Center, April 1985.
8. D. R. Kendall and J. S. Mills, "The Influence of JFTOT operating Parameters on The Assessments of Fuel Thermal Stability", SAE paper No. 851871, Society of Automotive Engineers, October 1985.
9. L. L. Stavinoha, J. G. Barbee, D. M. Yost, "Thermal Oxidative Stability of Diesel Fuels", Southwest Research Institute, Inc., BFLRF Report No. 205, February 1986.
10. S. D. Darrah, et.al., "Performance and Safety Characteristics of Improved and Alternate Fuels", Geo-Centers, Inc., Report No. GC-TR-86-1601, December 1986.

11. R. N. Hazlett, J. M. Hall and M. Matson, "Reactions of Aerated n-Dodecane Liquid Flowing over Heated Metal Tubes", Ind. Eng. Chem. Prod. Res. Dev., (16), No.2, p.171, 1977.

Table 1 - JFTOT Heater Tube Deposit Measurements

Total Carbon, micrograms	Total Delta TDR	Volume, cu.mm.	
		Interferometry	Dielectric Breakdown
876.8	965		0.6365
587.9	819		0.4570
537.3	628		0.4553
514.9	790		0.4962
456.2	731		0.4129
430.8	772		0.4057
398.5	685		0.4272
385.2	476		0.4149
381.2	634	0.350	0.3752
321.8	612	0.310	0.2627
304.1	672	0.330	0.3493
237.6	594	0.260	0.2182
163.4	374	0.190	0.1563
158.4	283	0.110	0.1238
91.2	494	0.086	0.0545
83.6	626		
59.4	317	0.055	0.0237
55.8	345	0.067	0.0281
52.0	445	0.053	0.0233
50.7	419	0.041	0.0309
47.0	355	0.041	0.0194
39.6	150	0.028	0.0129
27.2	299	0.016	0.0086

Table 2 - Linear Correlation Coefficients from Comparisons of  
Post-Run JFTOT Heater Tube Deposit Evaluation Methods

Independent Variable	Dependent Variable	Correlation
Total Carbon	Dielectric Volume	0.974
Total Carbon	Optical Volume	0.971
Optical Volume	Dielectric Volume	0.970
Total Delta TDR	Total Carbon	0.748
Total Delta TDR	Dielectric Volume	0.729
Total Delta TDR	Optical Volume	0.707

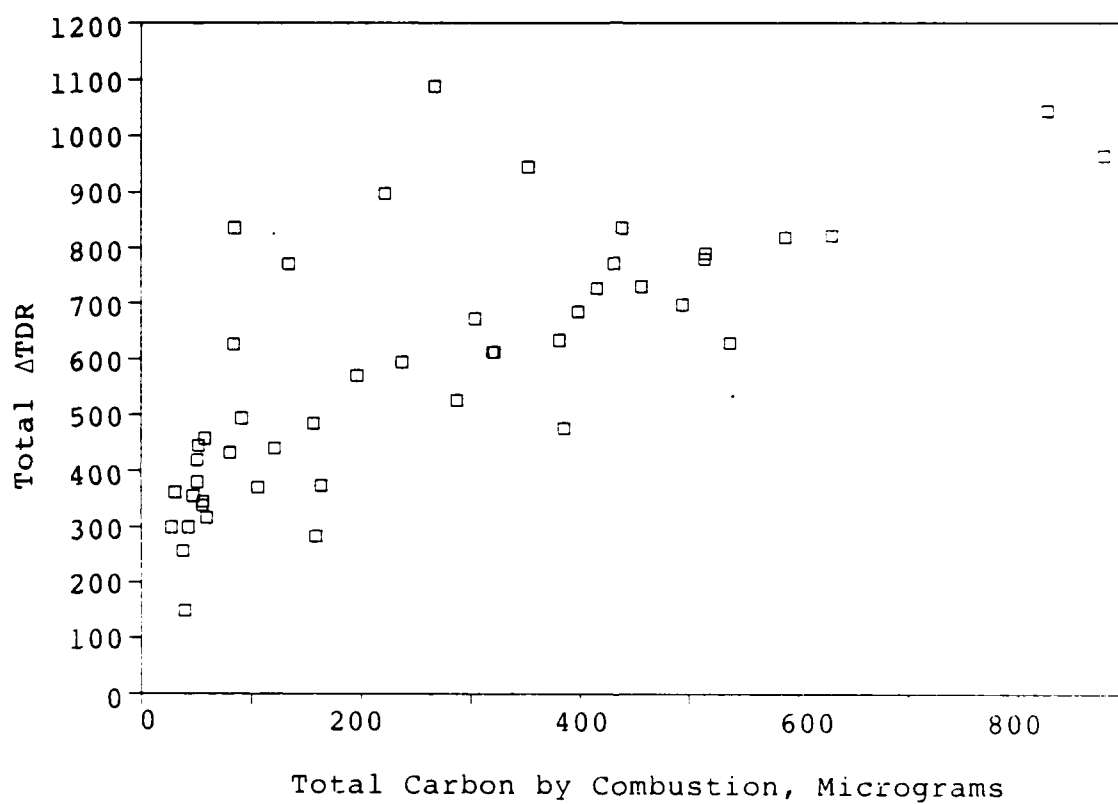


Fig. 1. Total Carbon vs Total  $\Delta TDR$

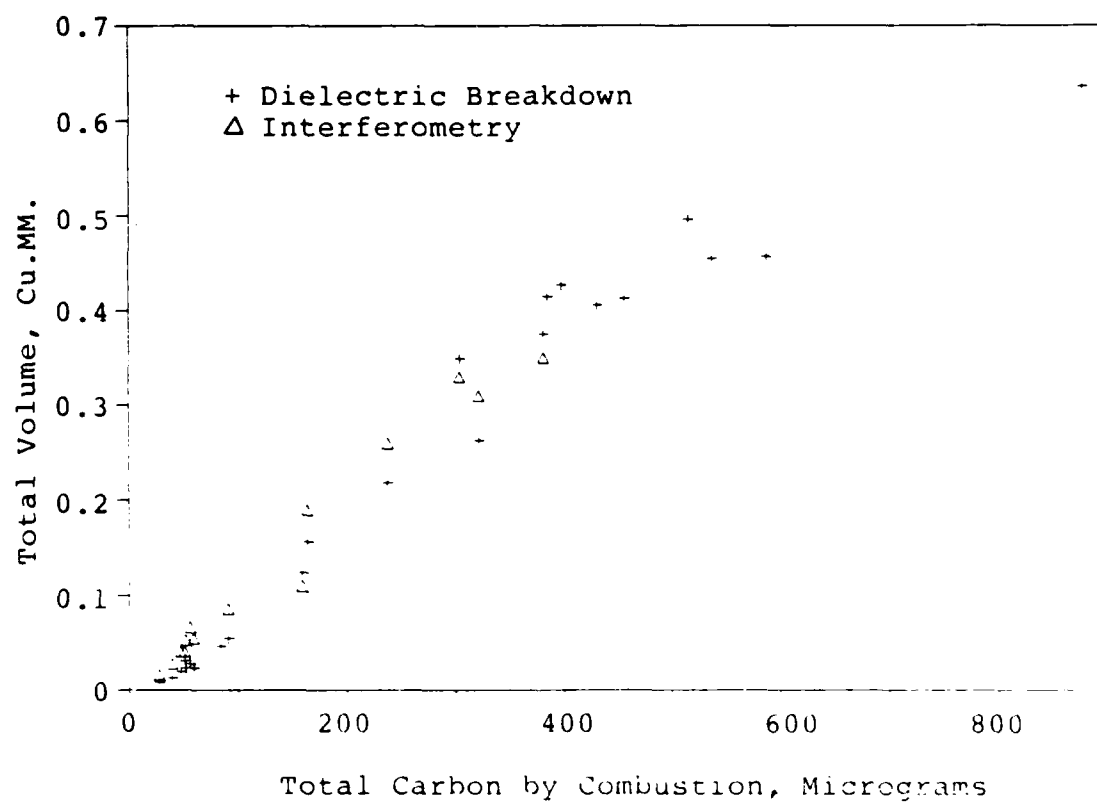


Fig. 2. Total Carbon vs Deposit Volume



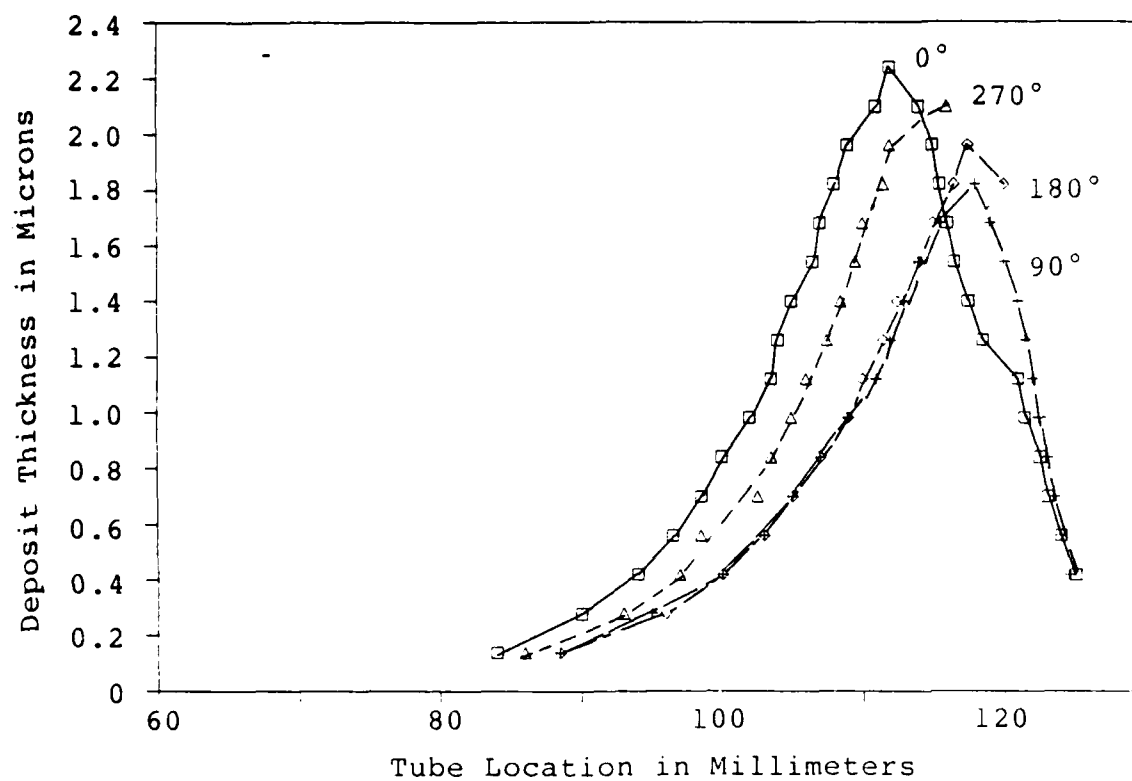


Fig. 3. Post-Run Spatial Measurements of Deposit Thickness by Interferometry Along Four Sides of the Tube

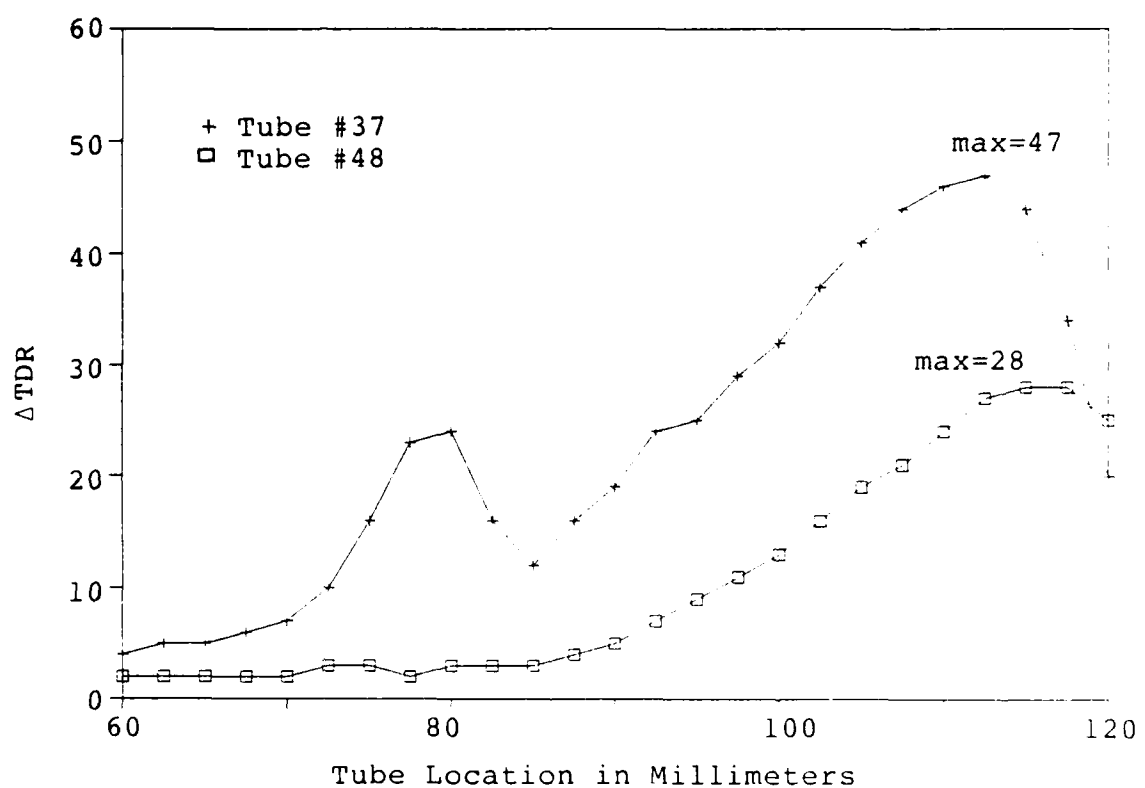


Fig. 4. Post-Run Spatial Measurements by Spun TDR

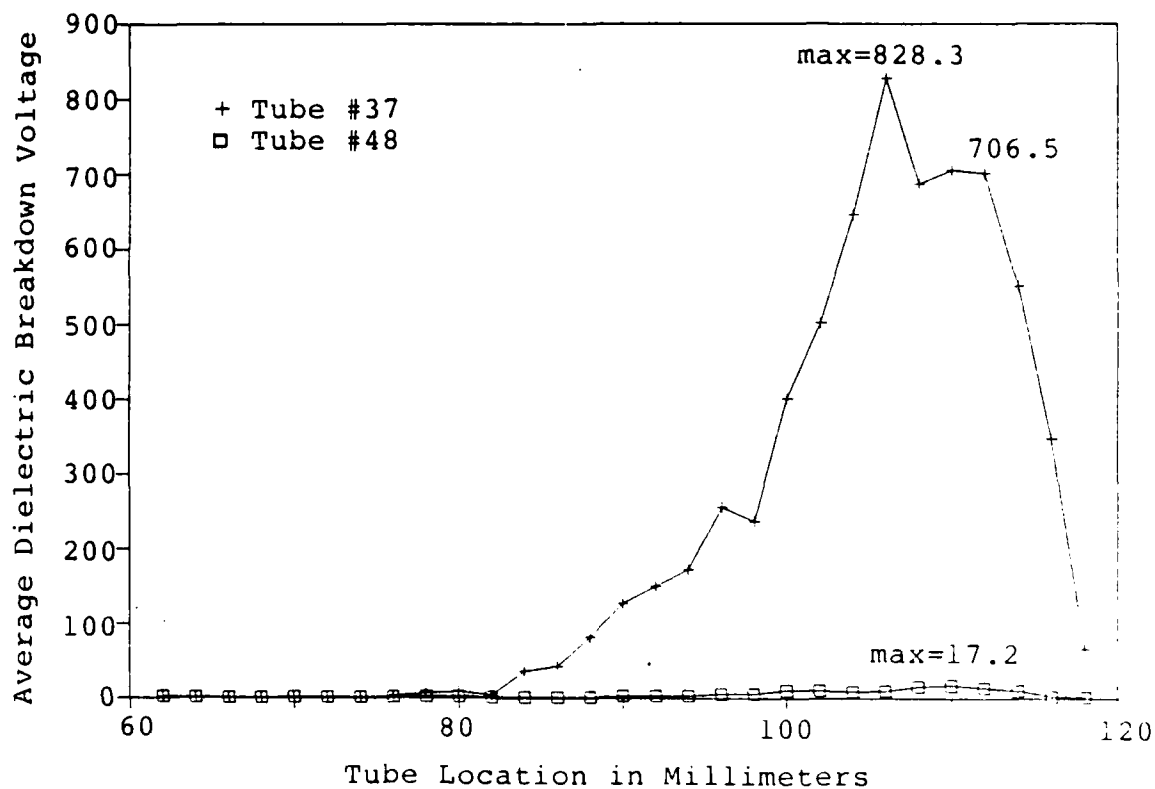


Fig. 5. Post-Run Spatial Measurements by Dielectric Breakdown

END

3-88

DTIC